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(54) Title: POLYMER HAIR FIXATIVES (57) Abstract The present invention relates to hair fixatives: (1) a terpolymer hair fixative comprising vinyl caprolactam, vinyl pyrrolidone and methacryloamidopropyl trimethylammonium chloride; or (2) vinyl caprolactam, vinyl pyrrolidone, dimethylaminoethyl methacrylate and acrylic acid; (3) vinyl caprolactam, vinyl pyrrolidone and vinyl acetate; and (4) a process of making a monomer mixture of maleic anhydride, vinyl acetate and isobornyl acrylate or methacrylate.		

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POLYMER HAIR FIXATIVES

The present invention relates to hair fixatives:

(1) a terpolymer hair fixative comprising vinyl caprolactam, vinyl pyrrolidone and methacryloamidopropyl trimethylammonium chloride; or (2) vinyl caprolactam, vinyl pyrrolidone, dimethylaminoethyl methacrylate and acrylic acid; (3) vinyl caprolactam, vinyl pyrrolidone and vinyl acetate; and (4) a process of making a monomer mixture of maleic anhydride, vinyl acetate and isobornyl acrylate or methacrylate.

(1) In one embodiment of the invention, the terpolymer hair fixatives of the present invention suitably comprise about 5-70%, preferably 10 to 30%, by weight of vinyl caprolactam, about 25-90%, preferably 35 to 70%, by weight of vinyl pyrrolidone and about 5-20%, preferably 10 to 15%, by weight of methylacryloamidopropyl trimethylammonium chloride.

These terpolymers are conveniently prepared in aqueous solution by subjecting the above monomers, either in admixture or while being added sequentially into a reactor, to a temperature of about 40° to 120°C., preferably 60 to 70°C., under agitation in an inert atmosphere, for a period of about 0.5 to 10 hours, in the presence of a free radical polymerization initiator or catalyst. Representative catalysts include organic and inorganic peroxides, e.g. hydrogen peroxide, Lupersol 11, or an azo compound, e.g. azobisisobutyronitrile, 2,2'-azobis-(2,4-dimethyl valeronitrile); although others known in the art may be used as well. Ordinarily the

aqueous solutions of the terpolymers thus- obtained are used as such for preparing water-based hair spray compositions which meet VOC regulations; however, if desired, the terpolymer product itself may be separated from the solution and recovered, for example, by evaporation of solvent, or other conventional method.

(2) Another embodiment provides a polymer hair fixative comprising 5-80% vinyl caprolactam (VCL), 25-90% vinyl pyrrolidone (VP), 2-15% dimethylaminoethyl methacrylate (DMAEMA) and 0.1-5% acrylic acid (AA), by weight of the polymer.

More particularly, the polymer hair fixatives (2) comprises about 5-80%, preferably 10 to 70%, by weight of vinyl caprolactam, about 25-90%, preferably 35 to 80%, by weight of vinyl pyrrolidone, about 2-15%, preferably 3 to 10%, by weight of dimethylaminoethyl methacrylate and 0.1-5%, preferably 0.5-2% by weight of acrylic acid.

The polymerization may be a run in 100% water solvent, or in mixtures of water and alcohol, e.g. isopropanol or ethanol, to provide polymer have specific viscosities of about 0.2-5, preferably about 0.5-2, and most preferably about 1.0. In 100% water, the specific viscosity of the polymer obtained is about 1.5 to 3.5, whereas in water-alcohol mixtures, the specific viscosities produced were about 0.3-1.5, generally about 0.4-1.2.

In water-alcohol mixtures, the reaction product can be stripped of alcohol to provide an all water composition.

The polymerization is run at a solids contents (of monomers) of about 10-40%, preferably 15-30%, and most preferably about 20%.

The residual VP content of the product is less than 0.1%, preferably less than 0.05% and most preferably 0%.

(3) The terpolymer hair fixatives can suitably comprise about 5-70% by weight of vinyl caprolactam, about 20-80% by weight of vinyl pyrrolidone and about 5-50% by weight of vinyl acetate.

Terpolymers comprising 5-30%, preferably 10-20%, VCL; 50-85%, preferably 70-80% VP; and 5-20%, preferably 10-15% VA, usually are prepared in aqueous or aqueous-alcoholic solution; whereas terpolymers comprising 10-70%, preferably 30-60%, VCL; 20-80%, preferably 20-50%, VP; and 5-50%, preferably 10-30%, VA usually are prepared in alcoholic solution.

The relative viscosity of the terpolymers produced in 100% water generally is in the range of about 2.5 to 4.8.

Alternatively, the terpolymers can be prepared in a mixture of water and an alcohol, i.e. isopropanol. In such mixed solvents, the preferred all-water product can be obtained by stripping the alcohol and replacing it with water. The relative viscosity of the terpolymer decreases as the ratio of alcohol-to-water increases.

The terpolymers also can be made in an all-alcoholic solvent, i.e. ethanol or isopropanol; in such solvent the relative viscosity of the terpolymer is about 1.2-1.5.

(4) The terpolymer product is a random or alternating structure comprising essentially maleic anhydride, vinyl acetate and isobornyl acrylate or methacrylate. A typical terpolymer composition comprises the monomers, respectively, in a molar ratio of about

0.35-1:1:0.05-0.25, preferably 0.6-0.8:1:0.08-0.12, and, most preferably, 0.75:1:0.1, which are prepared by a solution polymerization process.

The process comprises adding the monomers, individually or premixed, preferably in the above proportions, in acetone solvent for both the monomers and the terpolymer, wherein they are polymerized in the presence of a free radical initiator under conditions of agitation at a temperature of between about 40° and about 90°C., preferably between about 50° and about 70°C. The initiator can be added to the monomer mixture before or after the monomers have been charged into the solution medium. The reaction is carried out under an inert atmosphere which can be maintained by purging with nitrogen to eliminate air and oxygen.

The polymerization reaction is carried under constant agitation over a period of from about 4 to 24 hours, although usually about 4 to 12 hours is sufficient to complete the reaction and form the terpolymer product. At this point, the terpolymer product, which is in the form of the free maleic acid product, can be esterified, hydrolyzed or neutralized. Preferably, the terpolymer is esterified with a C₄-C₅ alkanol, such as butanol or pentanol, to provide the corresponding mono-butyl maleate derivative. Alternatively, the terpolymer can be hydrolyzed or neutralized, if desired.

The invention will now be described with reference to the following examples.

Embodiment (1)EXAMPLES 1-17PREPARATION OF VCL/VP/MAPTAC
TERPOLYMERS IN AQUEOUS SOLUTION

A one-liter glass resin kettle, fitted with an anchor agitator, a temperature controller, a nitrogen inlet, a monomer feed tube and a condenser, was charged with VCL and distilled water. The solution in the kettle then was purged with nitrogen for 30 minutes with the dip tube was positioned at the bottom of the reactor. The nitrogen flow was continued and the dip tube was raised above the solution. The solution then was heated to 65°C. and a feed of VP/MAPTAC* monomers was pumped into the kettle at a rate such that the feed was completed in 2 hours. The start of addition of the feed was considered to be time zero. A first initiator charge of Lupersol 11 was added at time 10 minutes, a second shot of the same amount at 60 minutes, and the remaining third at the completion of the monomer feed. The total addition took approximately 120 minutes whereafter 0.8 g. of initiator had been added. The reaction mixture then was held at 65°C. for an additional 3 hours, heated to 90°C. and 1 g. of t-butyl peroctoate (Triganox 21) was added as an additional initiator. The reaction mixture was maintained at 90°C. for 8 hours, cooled and discharged.

* MAPTAC is available from The Virginia Carolina Chemicals Company as methacrylamidopropyl trimethylammonium chloride

The several VCL/VP/MAPTAC terpolymers produced by this process are given in Table I below.

TABLE I
PREPARATION OF VCL/VP/MAPTAC TERPOLYMERS IN AQUEOUS SOLUTION

EX. NO.	VCL (g)	VP (g)	MAPTAC* (g)	WATER** (g)	WEIGHT RATIO VCL/VP/ MAPTAC
1	5	90	5	455	5/90/5
2	10	85	5	455	10/85/5
3	15	80	5	455	15/80/5
4	20	75	5	455	20/75/5
5	5	90	10	460	5/85/10
6	5	90	10	460	5/85/10
7	10	85	10	460	10/80/10
8	15	80	10	460	15/75/10
9	20	75	10	460	20/70/10
10	5	80	15	465	5/80/15
11	5	80	15	465	5/80/5
12	10	75	15	465	10/75/15
13	10	75	15	465	10/75/15
14	15	70	15	465	15/70/15
15	15	70	15	465	15/70/15
16	20	65	15	465	20/65/20
17	20	65	15	465	20/65/15

* MAPTAC - added as 50% Aqueous Solution

** Water - Includes water in MAPTAC Solution

The properties of the aqueous solutions of the VCL/VP/MAPTAC terpolymers produced above are presented in Table II below.

TABLE II

CHARACTERIZATION OF AQUEOUS SOLUTIONS
OF VCL/VP/MAPTAC TERPOLYMERS

<u>EX. NO.</u>	<u>% SOLIDS</u>	<u>pH</u>	<u>RELATIVE</u> <u>VISCOSITY</u>	<u>% RESIDUAL</u> <u>VP</u>
1	20.04	4.81	2.51	0.0
2	20.11	4.13	2.07	0.0
3	17.73	3.95	2.01	0.0
4	24.41	3.96	2.41	0.02
5	19.48	4.62	3.39	0.0
6	21.87	4.21	3.56	0.02
7	20.20	4.48	4.13	0.02
8	22.41	5.02	4.31	0.03
9	20.02	5.18	4.22	0.0
10	24.08	5.67	5.98	0.015
11	20.09	4.34	5.41	0.0
12	19.10	5.53	4.79	0.015
13	17.66	4.46	4.56	0.0
14	18.38	5.05	4.53	0.01
15	22.87	4.45	5.45	0.0
16	20.00	4.91	3.24	0.0
17	17.45	4.55	4.50	0.0

As shown in Tables I and II, terpolymer containing three weight levels of MAPTAC were prepared, namely, 5%, 10%, and 15% by weight. At each concentration of MAPTAC, the VCL/VP ratio in the terpolymer was varied, the VCL content increasing from 5 to 20% by weight. For the series with 5% MAPTAC, the pH of the aqueous solution ranged from 3.95 to 4.81, the relative viscosity was 2.01 to 2.51, and the % VP residual was essentially zero. The pH for the series with 10% MAPTAC was 4.2 to 5.2, the relative viscosity was 3.56-4.31, and the % VP residual also was essentially zero. For the series with 15% MAPTAC, the pH range was 4.3 to 5.7; the relative viscosity was 3.24 to 5.98; residual VP again was absent from the product. Accordingly, increasing the % MAPTAC in the terpolymer resulted in an increase in the relative viscosity of the product, the pH remained essentially constant, and the residual VP content was essentially zero.

The water-based hair spray compositions of the invention containing the terpolymer hair fixative of VCL/VP/MAPTAC suitably comprises about 2 to 10%, preferably 3 to 6%, by weight of the terpolymer, about 10 to 60%, preferably 15 to 50%, by weight of water, about 20 to 40%, preferably 30 to 35%, by weight of dimethylether, and 0 to 15%, preferably 0 to 10%, by weight of ethanol. Such compositions are one-phase systems, can be made directly from the terpolymer solutions prepared by the aqueous solution process, meet VOC standards, and exhibit excellent performance characteristics in use as a hair spray.

While the mechanism of synergistic action of the three components of the terpolymer of the invention is not completely understood at present, it is believed that the presence of the VCL monomer therein provides a hydrophobic component which enhances the humidity resistance and hold of the hair spray composition while retaining the desired water solubility of the terpolymer and allowing its preparation by an aqueous solution process.

EXAMPLE 18PREPARATION AND EVALUATION OF
WATER-BASED HAIR SPRAY COMPOSITIONS

The following water-based hair spray formulations was prepared:

Terpolymer solution 20% solids (Ex. 2)	10 g.
Water-distilled	45
Ethanol-anhydrous	10
Dimethylether	35
	<hr/>
	100 g.

The formulation was tested in the conventional manner for hold (curl retention at 90% RH and 80°F.) showed 85% average % curl retention after 90 minutes of treatment.

EXAMPLE 19

Terpolymer solution (Exs. 2, 3 or 4)	10 g.
Water-distilled	55
Dimethylether	35
	<hr/>
	100 g.

These compositions showed a 70% curl retention after 90 minutes.

EXAMPLES 20-31PREPARATION OF VCL/VP/DMAEMA/AA
POLYMERS IN AQUEOUS-BASED SOLUTION

A one-liter glass resin kettle, fitted with an anchor agitator, a temperature controller, a nitrogen inlet, a monomer feed tube and a condenser, was charged with VCL and distilled water. The solution in the kettle then was purged with nitrogen for 30 minutes with the dip tube positioned at the bottom of the reactor. The nitrogen flow was continued and the dip tube was raised above the solution. The solution then was heated to 65°C. and a feed of VP/DMAEMA monomers and sodium acrylate were pumped into the kettle at a rate such that the feeds were completed in 2 hours. The start of addition of the feed was considered to be time zero. A first initiator charge of Lupersol 11 was added at time 10 minutes, a second shot of the same amount at 60 minutes, and the remaining third at the completion of the monomer feed. The total addition took approximately 120 minutes whereafter 0.8 g. of initiator had been added. The reaction mixture then was held at 65°C. for an additional 3 hours, heated to 90°C. and 1 g. of t-butyl peroctoate (Triganox 21) was added as an additional initiator. The reaction mixture was maintained at 90°C. for 8 hours, cooled and discharged.

The several VCL/VP/DMAEMA/AA polymers produced according to this general method are summarized in Table III below.

In the examples where an aqueous-alcoholic solvent was used, the alcohol was stripped off to provide an all water product.

TABLE III

PREPARATION OF VCL/VP/DMAEMA/AA POLYMERS IN AQUEOUS-BASED SOLUTION

<u>EX. NO.</u>	<u>VCL</u> <u>(g)</u>	<u>VP</u> <u>(g)</u>	<u>DMAEMA</u> <u>(g)</u>	<u>AA</u> <u>(g)</u>	<u>SOLVENT</u>	<u>PRODUCT</u>
20	10	85	5	1	W-100	Clear
21	10	85	5	1	W-50 I-50	Clear
22	10	85	5	1	W-90 I-10	Clear
23	10	85	5	1	W-75 I-25	Clear
24	10	85	5	1	W-50 E-50	Clear
25	10	85	5	2	W-100	Clear
26	20	75	5	1	W-50 I-50	Clear
27	30	65	5	1	W-50 I-50	Clear
28	40	55	5	1	W-50 I-50	Clear
29	50	45	5	1	W-50 I-50	Clear
30	60	35	5	1	W-50 I-50	Clear
31	70	25	5	1	W-50 I-50	Clear

The properties of the aqueous-based solutions of the VCL/VP/DMAEMA/AA polymers produced above are presented in Table IV below.

TABLE IV

CHARACTERIZATION OF AQUEOUS AND AQUEOUS-ALCOHOLIC
SOLUTIONS OF VCL/VP/DMAEMA/AA POLYMERS

<u>EX. NO.</u>	<u>% SOLIDS</u>	<u>SPECIFIC</u> <u>VISCOSITY</u>	<u>% RESIDUAL</u> <u>VP</u>
20	18.52	2.65	0.07
21	36.73	0.55	0.11
22	20.52	1.16	0.18
23	20.20	0.58	0.10
24	20.32	0.67	0.03
25	18.83	2.34	0.08
26	19.71	0.47	0.06
27	29.60	0.33	0.10
28	19.60	0.42	0.09
29	19.60	0.36	0.10
30	22.15	0.35	0.08
31	20.02	0.39	0.09

The water-based hair spray compositions of the invention containing the polymer hair fixative of VCL/VP/DMAEMA/AA suitably comprises about 2 to 10%, preferably 3 to 6%, by weight of the polymer, about 10 to 60%, preferably 15 to 50%, by weight of water, about 20 to 40%, preferably 30 to 35%, by weight of dimethyl ether, and 0 to 15%, preferably 0 to 10%, by weight of ethanol. Such compositions are one-phase systems, can be made directly from the polymer solutions prepared by the aqueous solution process, meet VOC standards, and exhibit excellent performance characteristics in use as a hair spray.

While the mechanism of synergistic action of the four components of the polymer of the invention is not completely understood at present, it is believed that the presence of the VCL monomer therein provides a hydrophobic component which enhances the humidity resistance and hold of the hair spray composition, and the acrylic acid component further enhances the water solubility of the product, thus providing better removability after use.

EXAMPLE 32

PREPARATION AND EVALUATION OF WATER-BASED HAIR SPRAY COMPOSITIONS

The following water-based hair spray formulations was prepared:

Polymer solution, 20% solids (Ex. 21)	10 g.
Water-distilled	45
Ethanol-anhydrous	10
Dimethyl ether	35
	<hr/>
	100 g.

The formulation was tested in the conventional manner for hold (curl retention at 90% RH and 80°F.) showed 85% average % curl retention after 90 minutes of treatment.

EXAMPLE 33

Polymer solution (Exs. 21, 22 or 23)	10 g.
Water-distilled	55
Dimethyl ether	35
	<hr/>
	100 g.

These compositions showed a 70% curl retention after 90 minutes.

EXAMPLES 34-43PREPARATION OF VCL/VP/VA TERPOLYMERS

A one-liter glass resin kettle, fitted with an anchor agitator, a temperature controller, a nitrogen inlet, a monomer feed tube, a reflux condenser, and a vacuum take-off was charged with VCL and solvent, i.e. distilled water, a mixture of water and isopropanol, or ethanol or isopropanol. The solution in the kettle then was purged with nitrogen for 30 minutes with the dip tube was positioned at the bottom of the reactor. The nitrogen flow was continued and the dip tube was raised above the solution. The solution then was heated to 65°C. and a feed of VP/VA monomers was pumped into the kettle at a rate such that the feed was completed in 2 hours. The start of addition of the feed was considered to be time zero. A first initiator charge of Lupersol 11 was added at time 10 minutes, a second shot of the same amount at 60 minutes, and the remaining third at the completion of the monomer feed. The total addition took approximately 120 minutes whereafter 0.8 g. of initiator had been added. The reaction mixture then was held at 65°C. for 18 hours. The reaction mixture was then cooled and discharged.

The several VCL/VP/VA terpolymers produced by the processes are given in Table V below.

TABLE V

PREPARATION OF VCL/VP/VA TERPOLYMERS

EX. NO.	VCL (g)	VP (g)	VA (g)	WATER (g)	ISOPRO- PANOL	ETHANOL	TEMP (°C.)	APPEAR- ANCE OF SOLUTION
34	10	80	10	100	-	-	65	sl. hazy
35	15	75	10	100	-	-	65	sl. hazy
36	15	75	10	100	-	-	75	clear
37	20	70	10	100	-	-	65	hazy
38	15	75	10	90	10	-	65	hazy
39	15	75	10	75	25	-	65	sl. hazy
40	15	75	10	50	50	-	65	sl. hazy
41	50	40	10	-	100	-	65	high viscosity
42	50	40	10	-	-	100	65	sl. yell w clear
43	70	20	10	-	-	100	65	sl. yellow clear sl. yellow

The properties of the aqueous solutions of the VCL/VP/VA terpolymers produced above are presented in Table VI below.

TABLE VI

CHARACTERIZATION OF SOLUTIONS
OF VCL/VP/VA TERPOLYMERS

<u>EX. NO.</u>	<u>% SOLIDS</u>	<u>RELATIVE VISCOSITY</u>
34	—	—
35	19.31	2.68
36	20.70	3.84
37	—	—
38	19.38	2.36
39	19.15	1.67
40	18.75	1.35
41	56.03	1.49
42	20.74	1.26
43	20.91	1.25

The one-phase water-based hair spray compositions of the invention containing the terpolymer hair fixative of VCL/VP/VA terpolymers suitably comprises about 2 to 10%, preferably 3 to 6%, by weight of the terpolymer, about 10 to 60%, preferably 15 to 50%, by weight of water, about 20 to 40%, preferably 30 to 35%, by weight of dimethylether, and 0 to 15%, preferably 0 to 10%, by weight of ethanol.

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EXAMPLE 44PREPARATION AND EVALUATION OF
WATER-BASED HAIR SPRAY COMPOSITIONS

The following water-based hair spray formulations was prepared:

Terpolymer solution 20% solids (Ex. 35)	10 g.
Water-distilled	45
Ethanol-anhydrous	10
Dimethylether	35
	<hr/>
	100 g.

The formulation was tested in the conventional manner for hold (curl retention at 90% RH and 80°F.) showed 85% average % curl retention after 90 minutes of treatment.

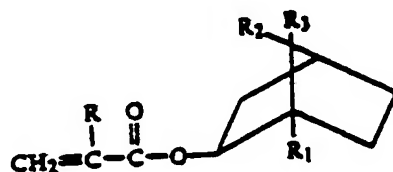
EXAMPLE 45

Terpolymer solution (Exs. 35, 36 or 37)	10 g.
Water-distilled	55
Dimethylether	35
	<hr/>
	100 g.

These compositions showed a 70% curl retention after 90 minutes.

(4) In this process, the vinyl acetate reactant may be substituted by other vinyl ester monomers. Examples of such vinyl ester monomeric components are those containing 4 to 14 carbon atoms which include vinyl acetate, vinyl propionate, vinyl isobutyrate, vinyl butyrate, vinyl hexanoate, vinyl pivalate, vinyl laurate and vinyl neodecanoate, of which vinyl acetate is the most preferred.

The isobornyl acrylate reactant may be substituted by other acrylate or methacrylate esters, of which suitably acrylate and/or methacrylate esters of isoborneol, exonorborneol and endo-norborneol are preferred, and the isobornyl ester is the most preferred. The preferred bicyclic compounds are those having a hydrocarbon bridge and are generally defined by the formula



wherein each of R, R₁, R₂ and R₃ is hydrogen or methyl.

The invention will now be described with reference to the following examples.

EXAMPLE 46

Into a four-necked, one-liter resin kettle, fitted with a nitrogen inlet tube, a dropping-funnel, a thermometer, a reflux condenser and a mechanical agitator, was charged 103.2 g. of vinyl acetate (1.2 moles), 154.8 g. of mono-n-butyl maleate (0.9 mole) and 24.96 g. of isobornyl acrylate (0.12 mole). After charging 0.2653 g. of di-ethylhexyl peroxydicarbonate (Lupersol® 223M75, 75% active) and 282.96 g. of acetone, the reactants were bubbled with nitrogen (150 ml/min.) for 15 minutes. The reactants then were heated gently under agitation (250 rpm) to 49°C. over 20 minutes and then to 58°C. over the next 10 minutes (mild reflux). The reaction was held at 58°-60°C. for 16 hours while adding 0.2653 g. of Lupersol® 223M75 hourly. At this point, unreacted vinyl acetate was 0.90% by titration. Then 282.96 g. of SDA-40-2 ethanol (95%) was added. Acetone was

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removed by distillation until the reactant temperature was 74°C. The terpolymer has a resin solids of 50.4%, a relative viscosity of 1.28 and a K value of 32.

The terpolymeric resins thus prepared by solution polymerization are employed as the active ingredient in a non-aerosol pump hair spray formulation and employed in a cosmetic product fitted with a suitable nozzle pump valve. The present resins are employed in concentrations between about 6 to 20% solids, preferably 8 to 15% solids. Such cosmetic products can be used over an extended period of time to generate fine spray mists without experiencing any nozzle clogging.

WHAT IS CLAIMED IS:

1. A polymer hair fixative comprising (1) vinyl caprolactam, vinyl pyrrolidone and methylacryloamidopropyl trimethylammonium chloride; (2) vinyl caprolactam, vinyl pyrrolidone, dimethylaminoethyl methacrylate and acrylic acid; (3) vinyl caprolactam, vinyl pyrrolidone and vinyl acetate or (4) a solution polymerization process for the preparation of terpolymers of maleic anhydride, vinyl acetate and isobornyl acrylate or methacrylate which comprises polymerizing said monomers in acetone solution.

2. A polymer hair fixative according to claim 1 in which (1) comprises about 5 to 70% by weight vinyl caprolactam, about 25 to 90% by weight vinyl pyrrolidone and about 5 to 20% by weight methylacryloamidopropyl trimethylammonium chloride.

3. An aqueous solution of the polymer of claim 1 wherein (1) has a solids content of about 15 to 30%, a pH of about 4 to 6, a relative viscosity of about 2 to 6, and a residual vinyl pyrrolidone level of less than about 0.03%.

4. A polymer hair fixative according to claim 1 in which (2) comprises about 5 to about 80% by weight vinyl caprolactam, about 25 to about 90% by weight vinyl pyrrolidone, about 2 to about 15% by weight dimethylaminoethyl methacrylate and about 0.1 to about 5% by weight of acrylic acid.

5. An aqueous or aqueous-alcoholic solution of the polymer of claim 1 wherein (2) has a solids content of about 10 to 40%, a specific viscosity of about 0.2 to 5, and a residual vinyl pyrrolidone level of less than about 0.1%.

6. A polymer hair fixative according to claim 1 in which (3) comprises about 5 to 70% by weight vinyl caprolactam, about 20 to 80% by weight vinyl pyrrolidone and about 5 to 50% by weight vinyl acetate.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US92/07012

A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) :A61K 7/06; 7/075

US CL :424/70

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 424/70, 71, 47

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 4,923,694 (SHIH ET AL) 08 MAY 1990 COLUMNS 2 & 3.	1-6
Y,P	US, A, 5,073,296 (KOPOLOW ET AL) 17 DECEMBER 1991; COLUMNS 3 & 4.	1-6
Y	US, A, 4,057,533 (HORT ET AL) 08 NOVEMBER 1977; SEE ENTIRE DOCUMENT	1-6
Y	US, A, 4,521,404 (LORENZ ET AL) 04 JUNE 1985 COLUMNS 5-8.	1-6

☐ Further documents are listed in the continuation of Box C.
 ☐ See patent family annex.

* Special categories of cited documents:	T	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
A document defining the general state of the art which is not considered to be part of particular relevance	X	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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O document referring to an oral disclosure, use, exhibition or other means		
P document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

08 OCTOBER 1992

Date of mailing of the international search report

Name and mailing address of the ISA/
Commissioner of Patents and Trademarks
Box PCT
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